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Future tasks in Interfacial electrochemistry and Surface reactivity.

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Interfacial electrochemistry is a main part of Physical Electrochemistry, which is developing in several directions. In this respect, this note will reflect my personal views in the "to do" list of topics related to well-defined interfacial electrochemistry and its application to the understanding of electrocatalytic reactivity, deliberately limited to single crystal platinum model electrodes in water electrolyte solutions. Several points are related to ongoing research and other have been suggested in meetings. Because of that, the text has a taste of *déjà vu*. References are a limited selection of examples for the interested readers.

In my opinion, it is clear that the main point to understand deals with the role of water at the interface. Water is not only the solvent but is a reagent taking part in the stoichiometry of most electrocatalytic processes. Water network is extremely sensitive to the electrolyte species [1, 2] that can modify the ability of water molecules to take part in electrode reactions. In the past, it was clear that anions may adsorb on the electrodes at potentials positive to the potential of zero charge (either free (pzfc) or total (pztc) in the Frumkin's approach [3]) and this strong interaction may mask the influence of anions as water structure makers or breakers [4]. On the other hand, it should be reminded that adsorption in electrochemistry is always competitive, as the adsorbates should displace water from the surface [5].

Recently, the role of cations, which are generally less specifically adsorbed, has been pointed out in many instances [6, 7]. However, in this case I am convinced that the effect is apparent and we are essentially observing the distortion of the water network caused by cations and its effect in reactivity. This is more evidenced in alkaline solutions, because the pztc is quite more negative than the pzfc [8].

On a less fundamental aspect, we have to define how charge influences in the acid-base properties of water itself [8] and the weak acids [9] present at the interface that will certainly influence in the adsorbed species that will compete with the reactivity of the molecules we are interested to study. We have to be conscious that there is a break of properties at the interface and a net charge at the metal side means an asymmetry in the distribution of cations and anions at the solution side and this has implications in the water network. The question also deals with the situation of absence of net charge, because it is know that the concentration of protons and hydroxide ions at the surface of water is not the same as in the bulk [10].

Incidentally, water ions move faster than any other ion in the electrolyte and we have to use fast perturbation techniques to address this problem that will certainly involve the relaxation of the water network after a short perturbation of the initial equilibrium state. Laser heating experiments have given important information about the interfacial properties of model single crystal electrodes, including composition and local properties [11, 12]. Incidentally, the data suggest the existence of a second pzfc as the electrode charge increases [13, 14] yet described by Frumkin on Pt black electrodes [3], which is related to the ability of platinum to dissociate water and change the composition of the surface at both sides of its "double layer" potential

range. The laser heating can be used to link interfacial charge, water reorganization and kinetics of relevant reactions [15]

Of course, dynamic experiments require extremely well controlled experimental conditions. The blank voltammetries, taken as fingerprint of the interfacial state, should have the best quality and be stable on time. One cannot gamble in this respect: if the quality of the stationary voltammogram is not the best, and one can distinguish quality just comparing literature data, all the following will be totally meaningless. To be strict, one should compare the blank voltammogram at the beginning with that at the end of the experiment and they should coincide.

At this moment we recall with a particularly important point, namely surface cleanliness, which is the most important since the use of solid electrodes was attempted [16, 17]. It is clear that single crystal work, were the number and properties of all surface atoms is known and should be in contact with the solution, require extremely clean surfaces and this requisite should also be fulfilled in electrocatalytic studies. One can argue that a *small* contamination could be acceptable because in electrocatalytic studies we are going to immerse our electrode, in an organic-containing solution and the high concentration of organic species will displace minor amounts of contaminants. This argument, claimed in the 90's is not acceptable now because the subtleties under scope require excellent data to get clear reactivity trends. If we want to understand reactivity we need the best defined electrochemical responses and thus the initial blank voltammogram should exhibit well-known characteristics. A simple inspection of the blank voltammogram enables to judge the quality of the experiment by comparing with well-known data published in the literature since 1980 [18, 19] and improving with expertise in the following years [20, 21].

It is obvious that this electrochemical characterization becomes difficult as soon as we deal with bimetallic electrodes, which are better catalysts than platinum in most cases [22, 23] but have a hydrogen region clearly modified in comparison with the pure metal. The characterization of the fingerprint voltammograms of bimetallic electrodes is certainly a challenge and is related to the modification of the mechanism of water dissociation on these electrodes. In any case, however, the zeroth-approach, the platinum substrate without modification should show the required characteristics to compare the effect of a second, or third.., component. If not, all the reported results are meaningless. To understand the electrochemical response of the surface of alloy materials is a very difficult task. I believe that the best method should be the transfer from Ultra High Vacuum (UHV) chamber to the Electrochemical cell, an experimental procedure widely used in the past [22, 23, 24]. The surface of the samples, e.g. composition and eventually surface order, can be precisely determined in UHV and then the electrode will be transferred to the EC, where the reactivity will be checked. After that, the electrode should be rinsed and removed back to the UHV chamber to see the eventual changes on the surface [25]. It is a very difficult experiment, but this would give valuable data about surface stability in the whole process. Of course, this bothersome procedure can be avoided by using robotics or when in-situ surface-electrochemical measurements can be carried out, but this approach may not be possible in all cases and certainly local probes will only give local information. The main difficulty would be again to maintain a clean interface in the whole time required by the experiment and because of that, it is important to examine the final state of the electrode.

A final reflection on the importance of this type of issues is that they deal with model electrode surfaces and the resulting experimental data that can be simulated by model

calculations. In the latter case, ideal surfaces of platinum are considered and the only way to check the results would be the comparison with experiments on the best, the closest to ideal, single crystal electrodes.

In summary, the future tasks should involve the understanding of the role of water at the interfaces as a fundamental molecular species. It is not only important that the solid is well controlled, we need to control dynamics in the solution side. I believe that this challenge will be the main issue of Physical Electrochemistry and Electrocatalysis in the future.

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